

Evaluation of Full Scale Stormwater Treatment Area Enhancements: Tracer Project

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Executive Summary

During 2003, a limerock berm was constructed in STA – 1W Cell 5b for purposes of enhancing the phosphorus removal performance of the wetland. The berm was constructed as part of an optimization effort performed by the South Florida Water Management District (District), with funding provided by the Florida Department of Environmental Protection (FDEP). DB Environmental, Inc. was selected by the District in 2004 to deploy a chemical tracer to assess the effects of the limerock berm on the hydraulic characteristics of Cell 5b. This document describes the methodology and results of the hydraulic characterization of this large (2,300 acre) submerged aquatic vegetation (SAV)-dominated wetland.

The field component of the tracer study was initiated on March 3, 2004, and completed two weeks later. Approximately 3,630 gallons of lithium chloride (LiCl) were utilized as the tracer, and this was distributed on a flow-weighted basis among the 22 Cell 5b inflow culverts. We monitored Cell 5b outflow Li concentrations at the ten outflow culverts, and we also performed internal monitoring at a network of pre-determined sampling stations to characterize the wetland hydraulic features. Key findings of this effort are as follows.

District-monitored water flows in Cell 5 demonstrated a close balance between wetland inflows and outflows, suggesting that seepage plays a minor role in the water budget. The complete recovery (104%) of the lithium at the wetland outflows also suggests little water is lost from the cell via seepage. Results of internal sampling demonstrated the presence of only minor short-circuits. The limerock berm, which was covered by 10 cm of water at the time of the study, did not redistribute water conveyed by these short circuits. The tracer response curves for the culvert outflows were bimodal, with a primary peak representing the injected tracer, and a secondary peak appearing several days later. Theoretical and empirical calculations demonstrate that this second peak represented “first peak” lithium from the Cell 5 discharge, that subsequently was conveyed out of STA-1W, northward in WCA-1 up the L7 canal, and then reintroduced into Cell 5.

We used an exponential decay model to extrapolate the tail of the first peak (which was masked by the second peak), and were therefore able to calculate several parameters that characterize

system hydraulics. The tracer recovery was 104% and the measured hydraulic retention time (HRT) was 4.35 days (compared to a nominal HRT of 4.15 days).

This study revealed that Cell 5b displays remarkably efficient hydraulic characteristics. For example, the tanks-in-series (TIS) value calculated for Cell 5b using the method of moments was 10.6, an extraordinarily high value when compared to previous assessments (TIS range of 1.3 – 3.4 for other STA-1W wetlands). This high hydraulic efficiency was depicted by the “near-plug-flow” shape of Cell 5b’s outflow tracer response curve, as well as the comparable export, on a mass basis, of lithium from the wetland’s 10 outflow culverts. Cell 5b’s high hydraulic efficiency is probably due to effective distribution of inflows among the 22 culverts at G-305, as well as the absence of pronounced short-circuit pathways. The limerock berm undoubtedly also plays a role in enhancing hydraulic performance of the wetland, but its exact contribution cannot be elucidated from the findings of this study.

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Introduction

During 2003, the South Florida Water Management District (District), with funding provided by the Florida Department of Environmental Protection (FDEP) under Grant Agreement Number G0040, constructed a limerock berm in Stormwater Treatment Area (STA) -1W, Cell 5b. This berm is thought to provide several benefits related to the phosphorus (P) removal capabilities of the wetland, including enhancing the system's hydraulic characteristics.

This final report summarizes the results of a hydraulic assessment in Cell 5b, using the tracer chemical lithium chloride (LiCl). The specific objectives of the project were to demonstrate and document the following:

- The ability of the limerock berm to improve the hydraulic distribution within treatment Cell 5b of STA -1W.
- Establish concentration and mass time series at each outflow culvert in order to characterize the inter-culvert variability of tracer mass distribution.

Project Location

STA-1W is located in western Palm Beach County (26° 38'N, 80° 25'W), 25 miles west of the city of West Palm Beach, Florida. This STA borders the northwest corner of Water Conservation Area 1 (WCA-1), the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Figure 1). The STA is a treatment wetland built on converted agricultural land previously farmed for sugar cane, corn and rice. The inflow structure into this STA is located at G-302. Flow then is split into three separate flow paths: the northern (Cells 5a and 5b), the western (Cells 2 and 4) and the eastern (Cells 1 and 3). The three flow paths then converge in the discharge canal, located along the western border, and water flows out of the STA through pump station G-310 (Figure 1). Water from the eastern flow path also can exit the STA via Pump station G-251.

This tracer study was conducted in Cell 5b, which has an effective treatment area of 2,293 acres. The inflow into this cell consists of 22 culverts at G-305. Water is discharged from 10 outflow culverts at G-306 (Figure 1).

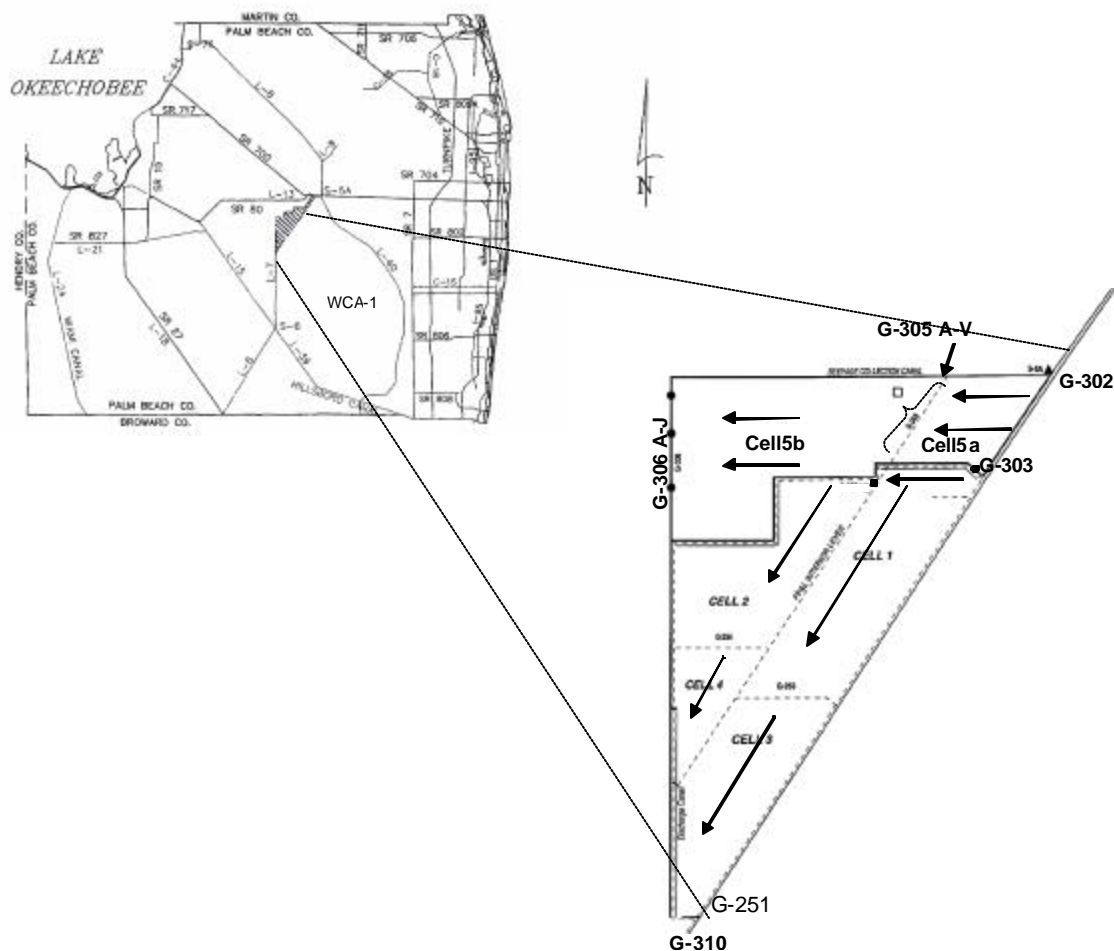


Figure 1. Location map of STA -1W.

Overview of Scope of Work

This project consisted of five tasks performed over a 25-week period. These included a Project Work Plan, Kickoff Meeting, the Tracer Project itself, Draft and Final Reports, and a Technical Review Meeting to present the findings of the study. This document represents the final report for this work effort.

For this hydraulic assessment, we injected a lithium tracer solution into Cell 5b using a flow-weighted distribution at the twenty-two (22) G-305 culverts. Monitoring at each of the ten (10) G-306 outflow culverts began immediately upon release of the tracer. Sampling was conducted for fourteen days, which was estimated to be sufficient time to capture the majority of the

injected lithium at the outflow culverts, i.e., after the peak concentration passed. Outflow sampling was conducted using time-proportional autosamplers. In addition, we performed three sampling events internal to Cell 5b to improve the District's ability to define potential hydraulic benefits provided by the limerock berm. Further details are provided in the Methodology Section.

This effort was managed by Ms. Lori Wenkert, Project Manager for the District, and by Mr. Thomas DeBusk, Project Manager for DBE. In addition, personnel from the firm Milian, Swain and Associates (MSA) assisted DBE with field and reporting efforts.

Methodology

Tracer Injection

We initially calculated that a total of 3665 gallons of 40% LiCl solution would be required to be injected among the 22 inflow culverts along the G-305 levee in Cell 5b (Figure 2) to achieve a continuously-stirred tank reactor (CSTR) concentration within the cell of 150 µg Li/L. This calculation, and assumptions upon which it is based, are provided in Appendix A. In order to identify potential flow variations among the 22 inflow culverts, the flow was measured on March 2, 2004 by adding a small amount of Rhodamine-WT™ dye tracer to the inflow end of each culvert. Velocity was measured by recording the time of transit of the dye cloud from the inflow injection side of the culvert to its outflow end (data located in Appendix B). Flow was then calculated as the product of velocity and the submerged cross-sectional area of the culvert. Using this information we were able to calculate the percentage of the total flow and the volume of lithium tracer to be added for each culvert (Table 1). The previous week, we had deployed small pools (4 ft diameter) adjacent to each culvert to serve as temporary LiCl reservoirs (Figure 3). On the morning of March 3, we filled these pools with the respective tracer volumes shown in Table 1. The original total tracer volume estimate was reduced to 3630 from 3665 gallons at this time, to ensure accurate allocation of the chemical among the 22 culvert reservoirs.



Figure 2. The STA-1W G-305 levee, which contains the 22 culverts into which the lithium tracer was injected. The levee separates Cell 5a (right) from Cell 5b (left).

Table 1. Percentage of total flow and calculated volume of Li tracer to be added to each culvert at G305.

| Culvert | Total Flow | Li Injected (gal) |
|----------------|-------------------|--------------------------|
| A | 3.3% | 121 |
| B | 3.1% | 114 |
| C | 4.3% | 155 |
| D | 3.7% | 134 |
| E | 3.8% | 140 |
| F | 3.7% | 134 |
| G | 4.2% | 152 |
| H | 4.7% | 171 |
| I | 4.0% | 145 |
| J | 3.9% | 143 |
| K | 4.4% | 161 |
| L | 5.4% | 195 |
| M | 5.0% | 181 |
| N | 6.1% | 220 |
| O | 5.2% | 189 |
| P | 5.1% | 185 |
| Q | 4.9% | 178 |
| R | 4.5% | 163 |
| S | 5.5% | 198 |
| T | 5.5% | 199 |
| U | 5.0% | 181 |
| V | 4.7% | 172 |
| Total | 100% | 3,630 |

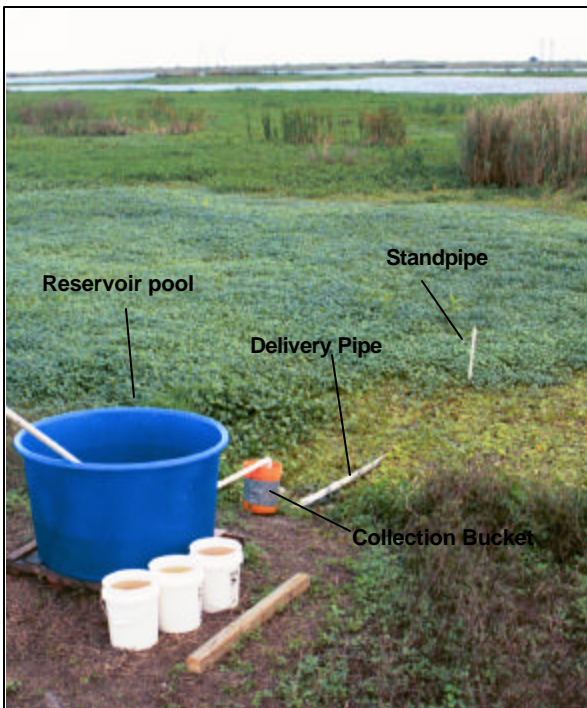


Figure 3. Photo depicting the tracer delivery infrastructure at one of the culverts at G-305. The tracer was injected into the upstream (east) end of each culvert. The standpipe, used as an air vent for the injection piping, is situated at the end of the submerged culvert.

On March 3 at 15:05, we initiated the tracer study by injecting the LiCl by gravity-feed from the reservoirs. We utilized a team of 9 field personnel to inject the tracer, with each person responsible for the delivery of the tracer at two or three adjacent culverts. We marked the commencement of tracer delivery to each culvert with a signal flare. Once the tracer injection was initiated at the first culvert, each of the 9 field personnel proceeded to their second assigned culvert, and initiated the application of tracer to the second culvert. Four of the 9 field personnel then proceeded to their designated third culvert and immediately released the tracer.

Because of the approximately 35.9 cfs flow rate of water transiting each culvert, we determined that there was no need to dilute the tracer beforehand. We calculated that a slow lithium delivery rate (0.00613 cfs per culvert) would provide more than ample dilution to disperse the tracer and prevent unequal downstream distribution of the tracer due to density effects. To further ensure adequate mixing of the relatively dense lithium chloride with the inflow waters, we slowly fed the tracer solution over a period of 1.5 to 2.25 hours, which produced a calculated negligible increase in specific gravity (1.00004) above that of pure water (1.00000 at 4 °C).

Outflow Monitoring

Each of the ten outflow culverts at G-306 was monitored using a time-discrete autosampler (single-stage programming sequence [ISCO Model 6712]). The uninterrupted operation of autosamplers at the outflow culverts was critical to the success of the project. Prior to the deployment of the lithium tracer, senior DBE and MSA personnel reviewed automatic sampler operational and maintenance protocols with the field technicians. On February 20 and 24, 2004 a 24-hr practice run was initiated with one-hour sampling frequency for each autosampler situated at the 10 outflow culverts. Except for a few missed samples caused by a battery failure, all tests were successful.

On March 2, 2004 a background lithium concentration sample was collected at each of the 10 outfall culverts. Once the tracer was injected on March 3, 2004 at 15:05, a sample was collected for each outfall every hour for the first two days, every-other-hour for the next two days, and every four hours for the remainder of the project. Of the total samples collected, 30% (30 per culvert) were analyzed for lithium. We submitted these samples for analysis in two batches. The first batch of 25 samples was sent for analysis and the results displayed as time series graphs from each culvert, and then submitted to the District for review. Based on review by our project team and the District Project Manager, a second batch of five samples was analyzed to fill in the time series where needed.

During the tracer project each automatic sampler was inspected four times daily during the time-critical first four days, with twice daily inspection provided for the remaining 10 days. Three backup autosamplers were kept on site in the event one of the original 10 autosamplers failed. Of a total of 1320 samples bottles collected over the two-week monitoring period, only three were not sampled properly by the autosamplers.

DBE personnel performed a rhodamine flow -calibration exercise, similar to the one performed for the G-305 inflow culverts, at each of the 10 outflow culverts of G-306 one day before the lithium tracer injection. The instantaneous rhodamine discharge was compared to the District's measured flow discharge at the same time. Subsequent to the lithium tracer injection, this effort was repeated at G-306 on March 5 and again on March 10, 2004 (days 2 and 7).

Internal Monitoring

To determine lithium tracer concentration profiles within the wetland, we performed internal water sampling by airboat utilizing two grids established within Cell 5b. Sampling of internal grids for lithium analyses was performed at 1, 3 and 7 days after tracer introduction. The first grid was comprised of 82 internal stations, situated equidistantly within the wetland (Figure 4). The dominant vegetation (presence/absence, and type) for this sampling grid was recorded for each station on February 20, 2004. The second sampling grid established within the wetland consisted of 50 stations situated within a hundred meters both upstream and downstream of the limerock berm (Figures 4 and 5). This finer resolution grid consisted of two north-to-south transects 25 and 50 m from the berm edge.

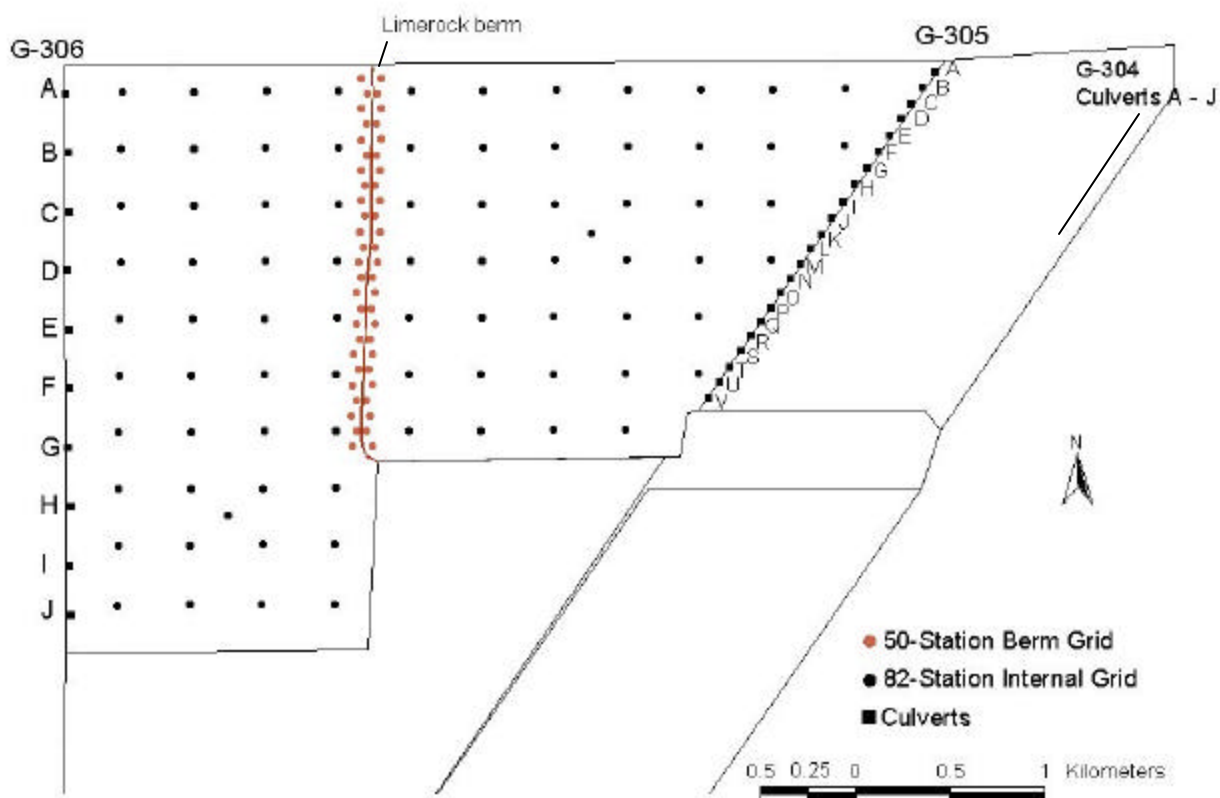


Figure 4. Location of internal lithium sampling stations within STA-1W Cell 5b. Letters denote inflow (G-305) and outflow (G-306) culverts.



Figure 5. Aerial photos of the limerock berm in Cell 5b. The berm was submerged under 10 cm of water during the tracer study.

Water samples were collected at a depth of 0.3 m in the water column, which was typically below the dense floating mat formed by the submerged macrophyte *Hydrilla verticillata* that dominates the wetland. On Day 3 we also collected surface Li samples to determine if *Hydrilla's* tendency to form dense floating mats at the water's surface affects the hydrology of the wetland by reducing the mixing of surface and bottom waters, thereby allowing water to “short-circuit” beneath the floating mat of vegetation.

Computations for Determining Hydraulic Parameters

Due to the unequal flow from the multiple discharge culverts at G-306, we flow-weighted the tracer concentration at each time step for G-306 prior to determining the following hydraulic parameters.

The nominal HRT, τ , is the volume of water in the treatment wetland (V) divided by the volumetric inflow rate of water (Q):

$$\tau = V/Q \quad (1)$$

The mean tracer residence time, τ_a , is defined as the average time that a tracer particle spends within a basin, and is the first moment of the residence time distribution (RTD) function. The RTD represents the time various fractions of water spend within a basin. It is the contact time distribution for the system and defines the key parameters that characterize the actual detention time (Kadlec 1994). Levenspiel (1989) uses the RTD in the analysis of reactor behavior. The mean residence time, τ_a , was calculated by dividing Eq. 4 of the tracer flow distribution, by Eq. 3, both of which are based on mean outflow rates and tracer concentrations (Kadlec 1994):

$$\tau_a = M_1/M_0 \quad (2)$$

$$M_0 = \int_0^{t_f} Q_e(t) C(t) dt \quad (3)$$

$$M_1 = \int_0^{t_f} t Q_e(t) C(t) dt \quad (4)$$

where $C(t)$ =exit tracer concentration (mg/m³); Q_e = flow rate (m³/d); t = elapsed time (d); and t_f = total time span of the outflow pulse (d).

Due to the unexpected appearance of a secondary Li peak, which became superimposed onto the descending limit of the primary peak, we extrapolated the descending limb according to an exponential decay function (Folger 1992). This produced a distinct profile and associated data set that was suitable for calculating the tracer recovery and HRT.

The parameter τ_a represents the centroid of the distribution and is the first moment of the RTD. The variance (σ^2) is the square of the spread of the distribution, or a measure of the dispersive processes, and is expressed in units of (time)²:

$$s^2 = \frac{\int_0^{t_f} t^2 Q_e(t) C(t) dt}{\int_0^{t_f} Q_e(t) C(t) dt} - \tau_a^2 \quad (5)$$

The variance, which is the second moment of the RTD, is particularly useful for matching experimental curves to one of a family of theoretical curves (Levenspiel 1972).

The variance can be rendered unit-less by dividing by the square of the tracer detention time:

$$s_{\Theta}^2 = \frac{s^2}{t_a^2} \quad (6)$$

where s_{Θ}^2 is the dimensionless variance of the tracer pulse.

Two common one-parameter models used to characterize non-ideal flows are the tank-in-series (TIS) and dispersion models (Levenspiel 1972). The TIS model views flow through a series of equal-size ideal stirred tanks, and the one parameter in this model is the number of tanks (N) in the chain. The number of constantly stirred tanks in the series that best matches the tracer response curve is given by N, which is determined by:

$$s_{\Theta}^2 = \frac{1}{N} \quad (7)$$

Results and Discussion

Hydraulic Conditions

During the tracer study the flow was kept relatively constant (Figure 6) and confined to the northern flow path of STA-1W (Cells 5a and 5b) (Table 2). District-reported flows averaged 774 cfs and 787 cfs for the Cell 5 inflow (G-304) and outflow (G-306), respectively.

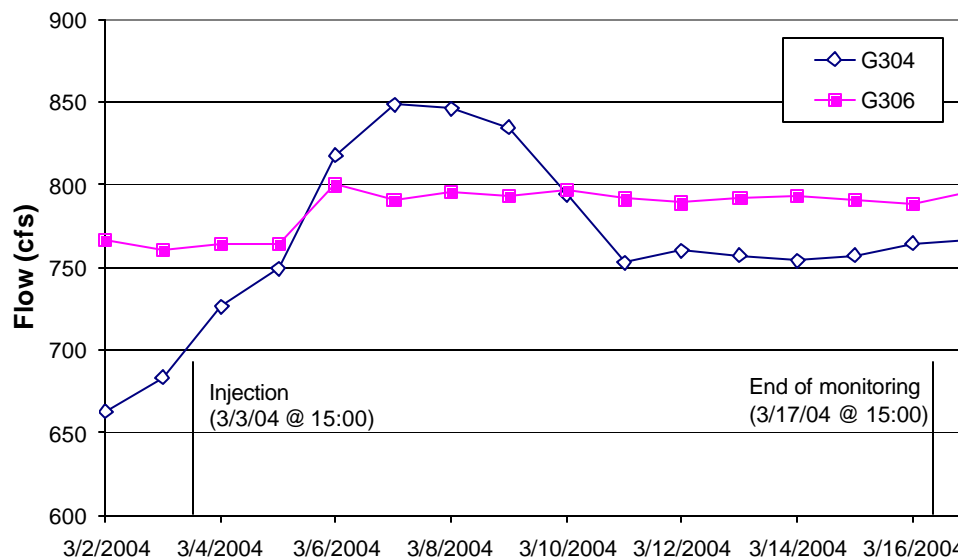


Figure 6. Flow rate for the inflow and outflow of Cell 5 (G-304 and G-306, respectively) during the tracer study (District data).

Table 2. Average daily flow summary in cubic feet per second (cfs) of structures in STA-1W during the tracer study in Cell 5b. All flow data provided by the District.

| Date | G302 | G301[†] | G310 | G251 | G304 | G306 | %G301 of G310 | %G301 of G302 | G303 | G308 | G256 | G309 |
|----------------|-------------|-------------------------|-------------|-------------|-------------|-------------|--------------------------|--------------------------|-------------|-------------|-------------|-------------|
| 3-Mar | 708 | 618 | 720 | 0 | 683 | 760 | 86% | 87% | 0 | 1 | 0 | 0 |
| 4-Mar | 743 | 667 | 718 | 0 | 726 | 765 | 93% | 90% | 0 | 0 | 0 | 0 |
| 5-Mar | 761 | 727 | 716 | 0 | 749 | 765 | 102% | 96% | 0 | 0 | 0 | 1 |
| 6-Mar | 808 | 809 | 722 | 0 | 818 | 800 | 112% | 100% | 0 | 0 | 0 | 0 |
| 7-Mar | 821 | 794 | 723 | 0 | 848 | 791 | 110% | 97% | 0 | 0 | 0 | 0 |
| 8-Mar | 821 | 726 | 728 | 0 | 846 | 796 | 100% | 88% | 0 | 0 | 0 | 0 |
| 9-Mar | 808 | 807 | 729 | 0 | 834 | 793 | 111% | 100% | 0 | 0 | 0 | 0 |
| 10-Mar | 776 | 702 | 730 | 0 | 794 | 796 | 96% | 90% | 0 | 0 | 0 | 0 |
| 11-Mar | 750 | 661 | 731 | 0 | 752 | 792 | 90% | 88% | 0 | 0 | 0 | 0 |
| 12-Mar | 757 | 593 | 730 | 0 | 760 | 789 | 81% | 78% | 0 | 0 | 0 | 0 |
| 13-Mar | 754 | 598 | 729 | 0 | 757 | 792 | 82% | 79% | 0 | 0 | 1 | 0 |
| 14-Mar | 753 | 605 | 729 | 0 | 755 | 793 | 83% | 80% | 0 | 0 | 1 | 0 |
| 15-Mar | 755 | 599 | 727 | 0 | 757 | 791 | 82% | 79% | 0 | 0 | 0 | 0 |
| 16-Mar | 758 | 607 | 726 | 0 | 764 | 788 | 84% | 80% | 0 | 0 | 0 | 0 |
| 17-Mar | 537 | 417 | 517 | 0 | 767 | 796 | 81% | 78% | 0 | 0 | 0 | 0 |
| Average | 756 | 662 | 714 | 0 | 774 | 787 | 93% | 87% | 0 | 0 | 0 | 0 |

[†] data provided as negative values and changed to positive for calculations.

DBE, Inc. and another consulting firm (Sutron, Inc.) performed flow calibration measurements at G-304, G-305, and G-306 both before and during the tracer-monitoring period. Each firm employed different flow measurement methods. DBE, Inc., injected rhodamine-WT dye at the entrance to each culvert along the G-305 and G-306 levees and recorded the time it took to transit the culvert lengths, whereas Sutron, Inc., employed an acoustic Doppler flow meter (ADFM) at the downstream end of the culverts. DBE's dye tracer method was an instantaneous measurement, whereas Sutron averaged flow measurements over 20-minute intervals at G-305 and G-306 and a 60-minute interval at G-304. For some culverts, flow measurements by each company were performed at the same time.

Although the measurements by DBE and Sutron were not performed on the same day for each of the 22 culverts at G-305, they were nevertheless made under similar flow conditions according to the hydrograph at G-304 (Figure 6). Agreement for the combined culvert flow was within 93% between the two independent measurements (Table 3). On one occasion (March 5, 2004), simultaneous flow measurements were performed by DBE and Sutron at three of the culverts at G-305, and agreement between the six pairs of side-by-side measurements ranged from 89 - 120% (Table 4). We are therefore confident that the combined culvert flow rate that we measured at G-305 one day prior to the injection of LiCl was accurate. This not only assures that the flow-weighted mass of LiCl injected at each culvert (Table 1) was valid, but also provides a flow measurement at an intermediate location (between Cell 5a and Cell 5b) not measured by the District.

There are two additional aspects of the hydraulic operations of the Cell 5b wetland that are important to note for this tracer study. First, historically there has been an apparent poor water balance for STA-1W Cell 5, with inflows substantially higher than outflows. The cause of this discrepancy was thought to be either extremely high seepage from the cell, or inaccurate readings from the non-calibrated structures at G-304 and/or G-306. Indeed, measurements by the District, Sutron and DBE at G-306 varied markedly at selected dates during the tracer study (Table 5). The District has since corrected the G-306 outflow data (using Sutron's calibrations), and the balance between corrected inflows (774 cfs) and outflows (787 cfs) during the study is

now quite close. The close agreement between inflow and outflow measurements demonstrates that seepage losses in Cell 5 were minimal during the study.

Table 3. Comparison of the instantaneous flow rates (dye tracer) on 3/2/04 with 20-minute mean acoustic Doppler flow meter (ADFM) flow rates measured within one week for the 22 culverts at G-305.

| Culvert | DBE Instantaneous Flow (cfs) | 20-Min Sutron ADFM Flow (cfs) |
|----------------|-------------------------------------|--------------------------------------|
| 305A | 27.5 | 29.7 |
| 305B | 26.0 | 33.1 |
| 305C | 35.3 | 33.4 |
| 305D | 23.4 | 21.3 |
| 305E | 25.4 | 24.0 |
| 305F | 26.1 | 23.2 |
| 305G | 30.0 | 26.0 |
| 305H | 34.6 | 28.3 |
| 305I | 25.2 | 26.2 |
| 305J | 26.1 | 24.0 |
| 305K | 32.8 | 29.6 |
| 305L | 41.9 | 38.3 |
| 305M | 34.3 | 25.7 |
| 305N | 46.7 | 35.9 |
| 305O | 41.8 | 33.8 |
| 305P | 37.5 | 37.7 |
| 305Q | 38.5 | 41.0 |
| 305R | 27.9 | 26.2 |
| 305S | 42.9 | 36.7 |
| 305T | 37.0 | 39.2 |
| 305U | 40.3 | 36.2 |
| 305V | 38.8 | 39.5 |
| Total | 740 | 689 |

Table 4. Comparison of the instantaneous flow rates (dye tracer) with the 20-minute mean acoustic Doppler flow meter (ADFM) flow rates measured simultaneously by DBE and Sutron, respectively, on March 5, 2004.

| Culvert | Date | Instantaneous | 20-min Sutron ADFM Flow |
|----------------|-------------|---------------------------------|--------------------------------|
| | | Rhodamine-WT™ Flow (cfs) | (cfs) |
| G305 Q | 3/5/2004 | 38.9 | 40.9 |
| G305 Q | 3/5/2004 | 37.2 | 41.2 |
| G305 R | 3/5/2004 | 33.6 | 27.8 |
| G305 R | 3/5/2004 | 30.3 | 25.3 |
| G305 S | 3/5/2004 | 46.8 | 42.0 |
| G305 S | 3/5/2004 | 45.4 | 40.3 |

Table 5. Comparison of the instantaneous tracer flow rates measured by DBE (dye tracer) and Sutron (20-minute mean acoustic Doppler flow meter (ADFM) rates) with the District's hourly flow rates for the 10 outflow culverts at G-306. Note that while District flows represent values from DBHydro, they are "uncorrected".

| Culvert | Date | Time | Instantaneous Rhodamine - WT Flow (cfs) | 20-Min Sutron ADFM Flow (cfs) | Hourly District Flow (cfs)‡ |
|----------------|-------------|---------------|--|--|--|
| G306 A | 03/02/04 | 14:29 | 58.9 | | 45.2 |
| G306 B | 03/02/04 | 14:21 | 75.0 | | 44.5 |
| G306 C | 03/02/04 | 14:13 | 62.3 | | 40.6 |
| G306 D | 03/02/04 | 14:03 | 73.5 | | 41.7 |
| G306 E | 03/02/04 | 13:55 | 59.3 | | 43.8 |
| G306 F | 03/02/04 | 13:45 | 52.9 | | 42.8 |
| G306 G | 03/02/04 | 13:33 | 71.5 | | 43.0 |
| G306 H† | 03/02/04 | 13:21 & 15:13 | 52.1 | | 42.6 |
| G306 I† | 03/02/04 | 13:11 & 15:05 | 48.3 | | 42.6 |
| G306 J | 03/02/04 | 14:46 | 65.0 | | 39.9 |
| Total | | | 619 | | 427 |
| G306 A | 03/05/04 | 11:05 | 40.0 | | 45.4 |
| G306 B | 03/05/04 | 10:07 | 52.5 | | 44.1 |
| G306 C | 03/05/04 | 10:15 | 53.3 | | 40.9 |
| G306 D | 03/05/04 | 10:25 | 58.3 | | 42.0 |
| G306 E† | 03/05/04 | 10:30 | 44.8 | | 43.7 |
| G306 F† | 03/05/04 | 10:42 | 40.1 | | 42.3 |
| G306 G | 03/05/04 | 10:55 | 53.6 | | 42.2 |
| G306 H† | 03/05/04 | 11:05 | 38.7 | | 42.0 |
| G306 I† | 03/05/04 | 11:25 | 39.5 | | 40.9 |
| G306 J | 03/05/04 | 11:35 | 43.6 | | 38.7 |
| Total | | | 464 | | 422 |
| G306 A | 03/10/04 | 14:35 | 46.5 | 75.2 | 43.8 |
| G306 B | 03/10/04 | 14:30 | 65.6 | 76.0 | 47.7 |
| G306 C | 03/10/04 | 13:50 | 56.5 | 75.8 [€] | 42.4 |
| G306 D | 03/10/04 | 13:40 | 72.1 | 92.4 | 43.6 |
| G306 E* | 03/10/04 | 13:25 | 54.9 | 71.9 | 45.5 |
| G306 F* | 03/10/04 | 14:45 | 50.7 | 70.4 | 45.3 |
| G306 G* | 03/10/04 | 15:00 | 65.1 | 77.3 | 45.4 |
| G306 H | 03/10/04 | 15:05 | 47.7 | 66.3 | 46.0 |
| G306 I | 03/10/04 | 15:10 | 52.1 | 74.1 | 45.0 |
| G306 J | 03/10/04 | 15:15 | 60.7 | 79.1 | 42.9 |
| Total | | | 572 | 758 | 448 |

‡ District hourly flow rate is based on the average value for the hour within which the rhodamine measurement was performed.

† Results based on the average of duplicate runs; if two times are not provided in the table, then the flow rate represents the mean of two consecutive measurements.

€ Average for remaining 9 culverts.

* Flows measured simultaneously by DBE and Sutron.

A second important hydraulic aspect relates to the source of water provided to Cell 5. In order to ensure a steady, moderate flow of water to STA-1W during the tracer study, the District capitalized on the higher stage of WCA-1, and provided flow by gravity from the conservation area through structure G-302. Pump station S-5A also was operated intermittently during this period, so the flows entering STA-1W were likely a mixture of water from the upstream watershed coupled with WCA-1 waters. The eastern and western flow paths of STA-1W were isolated from this flow by closing structure G-303, so that all flow passed through the G-304 structures to Cell 5. In order to ensure continued availability of water from WCA-1, the District also kept structure G-301 open, which allowed water to flow from southern portions of WCA-1 into its northern region, and then into STA-1W through G-302. This created the opportunity for a recirculation loop to develop, where water discharged from STA-1W through G-310 entered WCA-1, was conveyed northward through the L-7 canal along the western boundary of WCA-1, and then back into STA-1W through G-302 (Figure 7). The possibility of this recirculation pathway occurring was not immediately apparent to us, and was first identified by Dr. Michael Waldon of the Department of Interior upon review of our draft final report. The potential impact of this recirculation on the tracer findings is discussed later in this report.

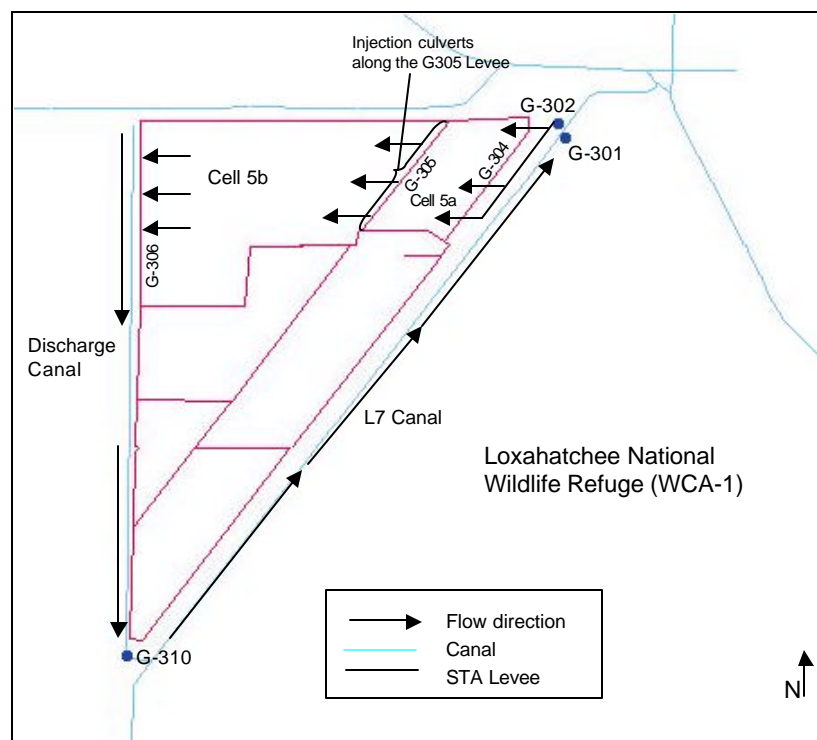


Figure 7. The use of WCA-1 as a water supply source created the possibility of a recirculation pathway between STA-1W and WCA-1 during the tracer study.

Time Series Progression of Tracer Movement

Figure 8 depicts the progression of lithium through Cell 5b over the course of the study. These maps were developed using the GIS mapping program ArcView Spatial Analyst. Since the limerock berm is a submerged permeable barrier (Figure 9), we chose to use the Spline/Tension method as the interpolation algorithm. This interpolation algorithm includes the lithium concentrations at nearby sampling sites on both sides of the berm when calculating concentration isopleths for the sampling areas on a given side of the berm.

Except for the southern-most culverts, the wetland water column adjacent to the G-305 inflow culverts returned to background lithium concentrations ($\sim 30 \mu\text{g/L}$) within one day after tracer injection (Figure 8). A combination of a shorter straight-line distance, a flow path with reduced vegetation densities, and higher discharges through these culverts (Table 1), likely explains why the Li tracer released two-thirds down the levee at G-305 (culverts O-S) reached the LR berm first. By day 3, nearly all of the tracer mass was located west of the LR berm, and all but two of the ten outflow culverts were exporting lithium at this time. In contrast, on day 7 lithium concentrations were higher on the east side of the LR berm than the west side (Figure 8), which is a reversal of the spatial concentrations observed on day 3.

We analyzed the lithium concentrations sampled at the surface and mid-depth (0.3 m) in the water column on day 3 to determine whether vertical concentration gradients existed. We found no such concentration gradient present (Figure 10), indicating that although preferred flow paths existed within the cell, blockage of vertical mixing by dense *Hydrilla* beds did not occur under this flow regime.

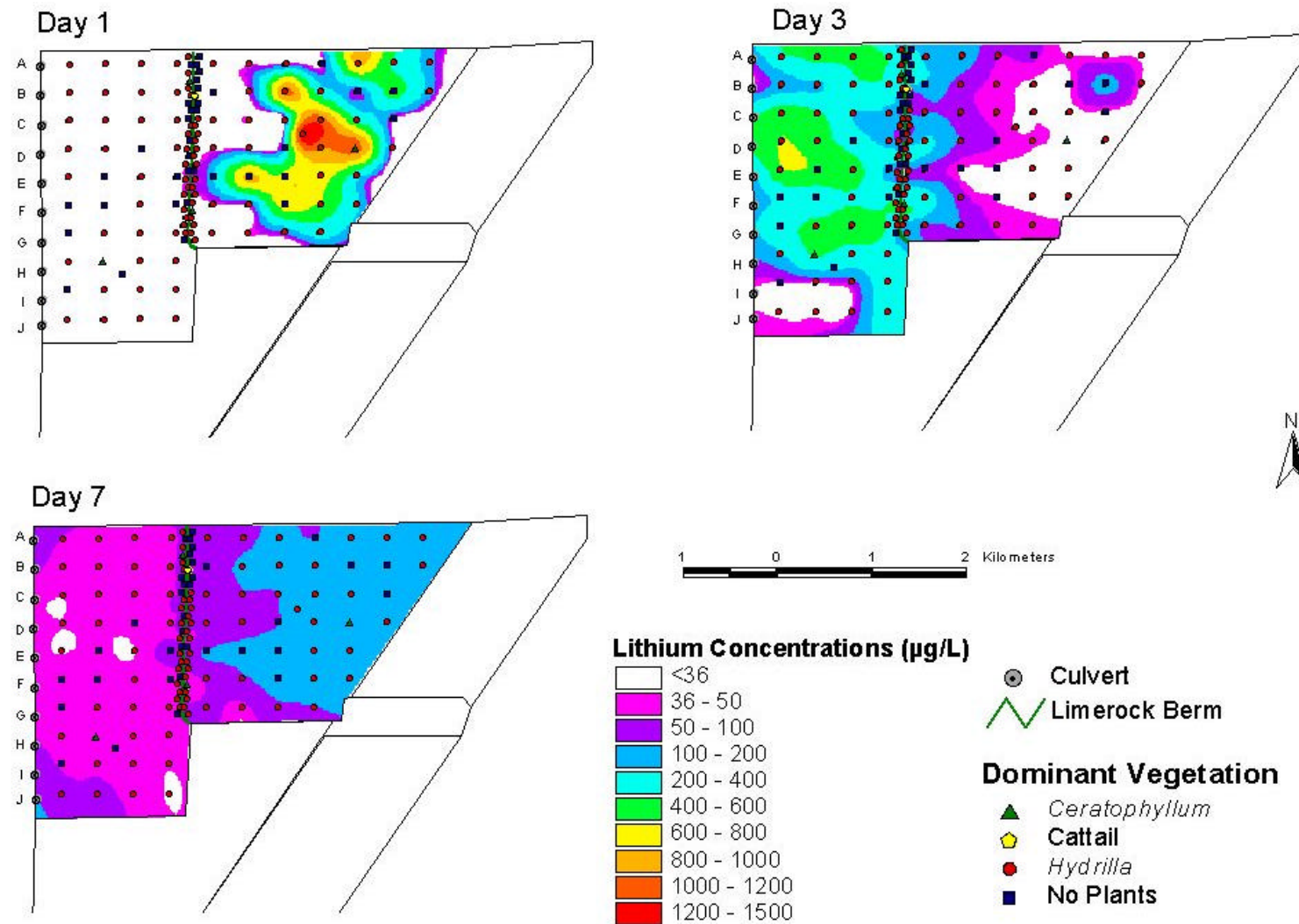


Figure 8 Two-dimensional spatial [Li] water column gradients one, three and seven days after injecting LiCl into Cell 5b at 22 culverts along the G-305 levee. Symbols are provided indicating the vegetation type where water samples were collected.



Figure 9. The limerock berm across Cell 5b on the third day (March 6, 2004) after LiCl injection. The water level is 10 cm above the top of the berm. Water stage on this day was 11.63 ft at G-305 and 10.74 ft at G-306.

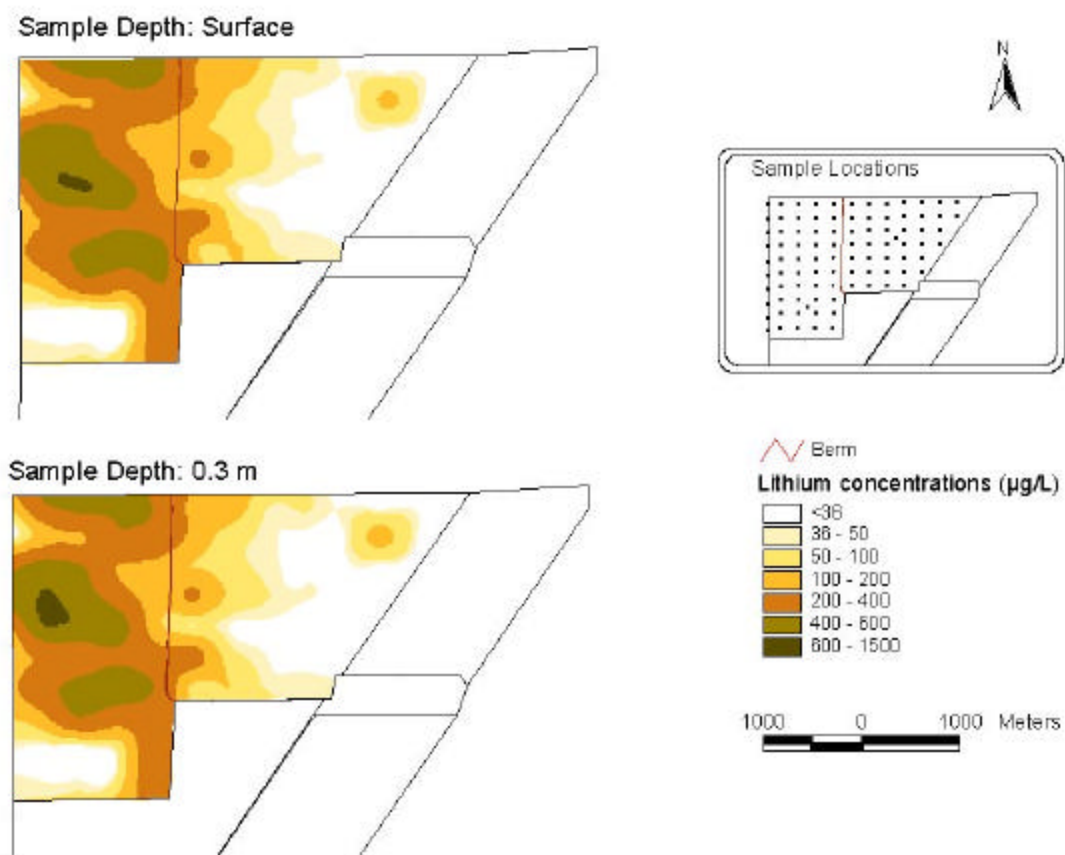


Figure 10. Two-dimensional spatial gradients comparing the lithium concentrations for water samples collected at the surface and mid-depth (0.3 m) in Cell 5b on the third day after LiCl was injected along the G-305 levee.

Flow-Weighted Tracer Response Curves

The first export of tracer from the cell at G-306 was observed at outflow culverts F and G (Table 6; Figure 11). By contrast, culverts C, D and E attained the highest peak outflow Li levels, with maximum Li concentrations greater than 400 µg/L. These culverts were in alignment with the high-concentration plumes west of the LR berm on day 3 (Figure 8). A secondary peak after day 9 was observed at all culverts (Figure 11), which probably was caused by recirculating tracer that was evident in the day 7 two-dimensional spatial concentration map (Figure 8).

We combined the flow-weighted tracer concentrations at each outflow culvert to produce a composited tracer response curve (Figure 12). In this composite curve, the first tracer breakthrough occurred at an elapsed time of 2 days, and peaked 32 hours later. The secondary peak that occurred after day 9 prolonged the HRT of the tracer within the cell such that the background lithium concentrations were not quite attained by the end of the 14-day study period (Figure 12).

Origin of the Secondary Peak

Based on chemical engineering textbook interpretations pertaining to chemical reactors (Levenspiel 1989), the bimodal Li tracer profile that appears during the tracer-monitoring period of March 3-17, 2004 in Cell 5b (Figure 12) suggests re-circulating pathway(s). However, other explanations for this secondary peak also are possible. These include inaccurate chemical analyses, inappropriate tracer injection methods, a spurious increase in background Li concentrations during the tracer study period, and non-equilibrium flow conditions resulting in the entrapment of tracer material in stagnant areas of the wetland which is then subsequently released at a later time during higher flows.

Table 6. Raw lithium concentration (µg/L) for samples collected during the tracer study at culverts G-306 A-J. The lithium tracer was injected on March 3, 2004. The samples collected on March 2, 2004 represent background concentrations.

| Sample Date/Time | ? T (days) | G-306A | G-306B | G-306C | G-306D | G-306E | G-306F | G-306G | G-306H | G-306I | G-306J |
|-----------------------------|-----------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 3/2/2004 | 0.00 | 29 | 28 | 29 | 31 | 30 | 29 | 29 | 28 | 29 | 29 |
| 3/3/2004 23:00 | 0.33 | 32 | 32 | 34 | 34 | 35 | 33 | 33 | 32 | 31 | 30 |
| 3/4/2004 7:00 | 0.67 | 33 | 32 | 34 | 35 | 35 | 33 | 34 | 33 | 31 | 30 |
| 3/4/2004 16:00 | 1.04 | 34 | 33 | 34 | 34 | 34 | 33 | 34 | 33 | 32 | 31 |
| 3/4/2004 23:00 | 1.33 | 33 | 33 | 33 | 34 | 35 | 33 | 33 | 35 | 32 | 32 |
| 3/5/2004 7:00 | 1.67 | 33 | 33 | 33 | 33 | 35 | 40 | 33 | 34 | 33 | 33 |
| 3/5/2004 15:00 | 2.00 | 33 | 33 | 32 | 32 | 34 | 78 | 49 | 37 | 34 | 32 |
| 3/5/2004 23:00 | 2.33 | 31 | 33 | 46 | 31 | 31 | 104 | 98 | 40 | 32 | 34 |
| 3/6/2004 7:00 | 2.67 | 33 | 33 | 155 | 106 | 38 | 117 | 156 | 34 | 33 | 33 |
| 3/6/2004 15:00 | 3.00 | 113 | 55 | 402 | 466 | 181 | 156 | 179 | 86 | 34 | 42 |
| 3/6/2004 23:00 | 3.33 | 303 | 88 | 439 | 537 | 567 | 271 | 237 | 147 | 34 | 179 |
| 3/7/2004 7:00 | 3.67 | 210 | 222 | 327 | 399 | 544 | 262 | 234 | 282 | 63 | 158 |
| 3/7/2004 15:00 | 4.00 | 376 | 302 | 240 | 224 | 384 | 224 | 216 | 374 | 104 | 159 |
| 3/8/2004 3:00 | 4.50 | 270 | 314 | 120 | 122 | 197 | 108 | 164 | 317 | 331 | 173 |
| 3/8/2004 15:00 | 5.00 | 234 | 214 | 84 | 84 | 97 | 66 | 126 | 277 | 334 | 155 |
| 3/9/2004 3:00 | 5.50 | 123 | 136 | 58 | 51 | 60 | 43 | 62 | 139 | 315 | 186 |
| 3/9/2004 15:00 | 6.00 | 95 | 95 | 48 | 48 | 51 | 45 | 60 | 81 | 192 | 215 |
| 3/10/2004 3:00 | 6.50 | 80 | 66 | 43 | 42 | 42 | 42 | 41 | 55 | 116 | 88 |
| 3/10/2004 15:00 | 7.00 | 62 | 54 | 40 | 40 | 39 | 43 | 43 | 55 | 81 | 103 |
| 3/11/2004 3:00 | 7.50 | 50 | 46 | 41 | 41 | 39 | 61 | 44 | 44 | 53 | 77 |
| 3/11/2004 15:00 | 8.00 | 51 | 44 | 50 | 48 | 43 | 69 | 63 | 43 | 48 | 57 |
| 3/12/2004 7:00 | 8.67 | 62 | 55 | 86 | 75 | 65 | 110 | 87 | 53 | 45 | 47 |
| 3/12/2004 19:00 | 9.17 | 94 | 74 | 107 | 118 | 86 | 92 | 100 | 61 | 45 | 44 |
| 3/13/2004 7:00 | 9.67 | 131 | 101 | 145 | 149 | 144 | 262 | 128 | 100 | 58 | 52 |
| 3/13/2004 19:00 | 10.17 | 132 | 125 | 142 | 138 | 138 | 129 | 117 | 115 | 69 | 68 |
| 3/14/2004 7:00 | 10.67 | 144 | 145 | 144 | 142 | 161 | 140 | 145 | 148 | 102 | 82 |
| 3/14/2004 23:00 | 11.33 | 125 | 130 | 107 | 109 | 125 | 111 | 107 | 120 | 109 | 89 |
| 3/15/2004 19:00 | 12.17 | 107 | 108 | 78 | 77 | 85 | 91 | 88 | 93 | 115 | 105 |
| 3/16/2004 7:00 | 12.67 | 86 | 106 | 69 | 74 | 83 | 88 | 85 | 94 | 135 | 126 |
| 3/17/2004 7:00 | 13.67 | 68 | 79 | 58 | 56 | 64 | 68 | 66 | 76 | 102 | 110 |
| 3/17/2004 15:00 | 14.00 | 63 | 66 | 52 | 54 | 52 | 56 | 55 | 61 | 81 | 95 |

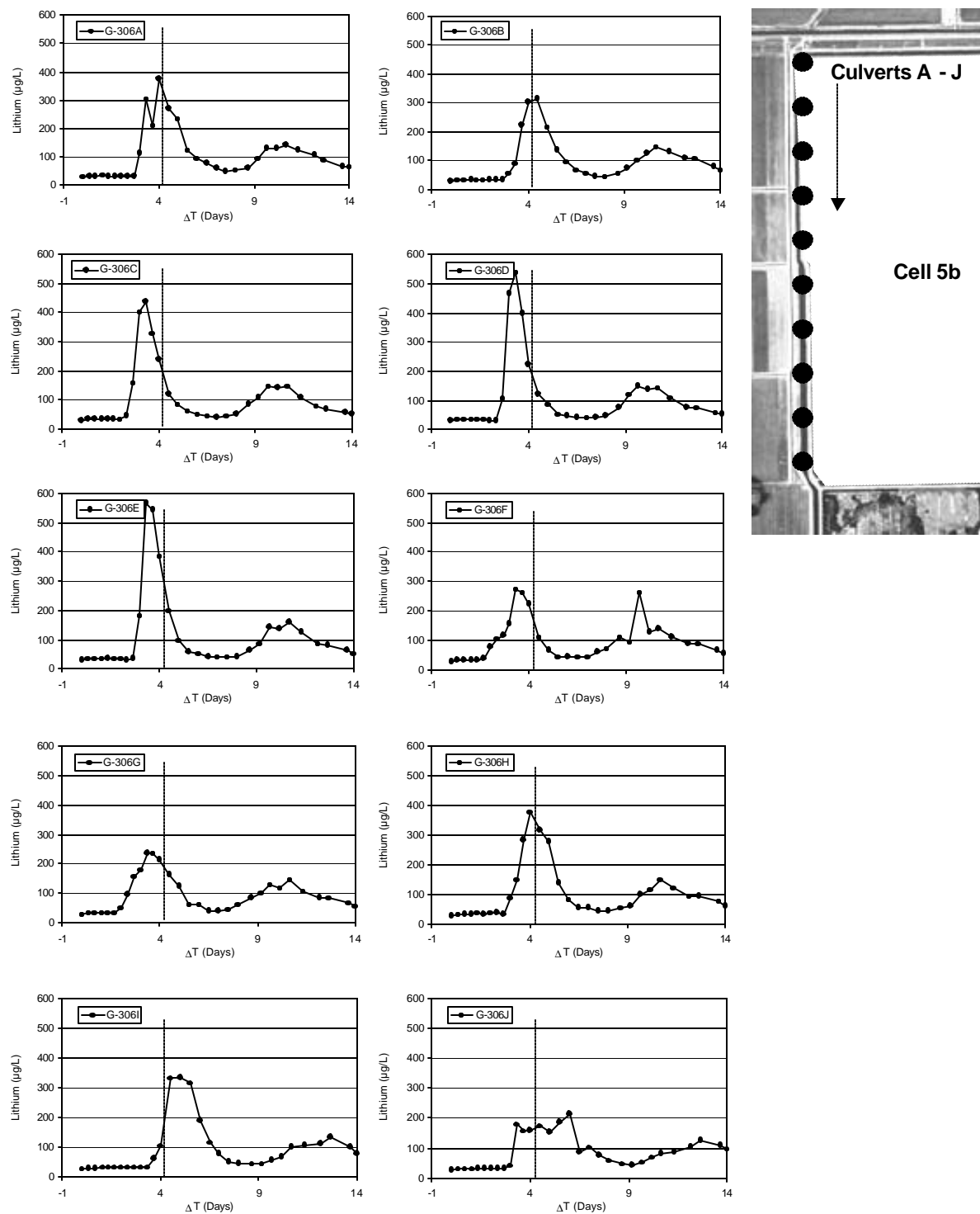


Figure 11. Tracer response curves for each of the 10 outflow culverts of Cell 5b along the G-306 levee. The data collection period was March 3 – 17, 2004. The vertical line located at 4.15 days is equal to the nominal hydraulic retention time.

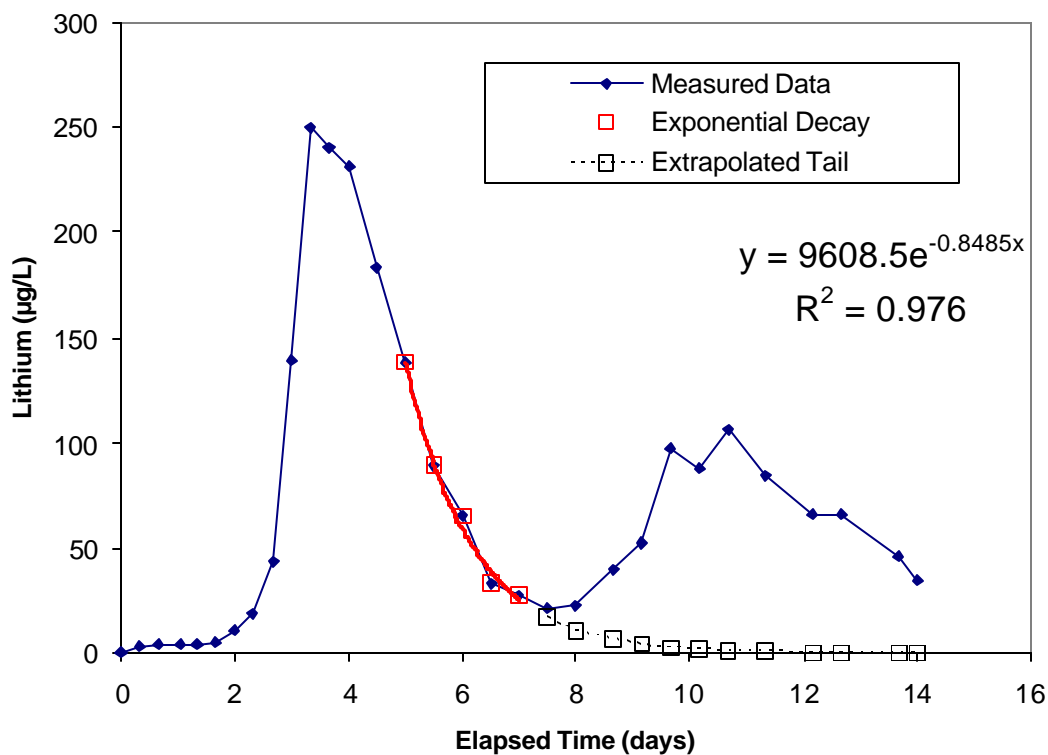


Figure 12. Flow-weighted tracer response curve for the combined 10 outflow culverts of Cell 5b along the G-306 levee. An exponential model was fit to the descending limb of the primary peak to extrapolate the tail.

To identify which of these explanations caused the appearance of the secondary peak in the tracer study, we examined the following theoretical and empirical data:

- density and mass balance calculations related to the tracer injection;
- calibration data from two independent sources for culvert flows at levees G-304, G-305, and G-306;
- historical background Li concentrations for STA-1W;
- split-sample, inter-laboratory comparison of Li concentrations collected during the tracer study;
- hydraulic aspects of the STA-1W and WCA-1 recirculation pathway.

Tracer Injection Methodology

Theoretical Density Calculations

We exercised caution in the injection of LiCl, which has a specific gravity of 1.20, to avoid the possibility of density stratification between the LiCl and receiving waters. The volume and velocity of the water moving through the culverts provided ample dilution (5000-fold) and energy to disperse the tracer, whose inflow point was carefully positioned under the surface of the water streaming through the culverts. We have calculated the specific gravity of the well-mixed tracer at the end of the culvert to be 1.00004, a value where temperature is likely to have more of an effect on specific gravity of the tracer than the salt content of tracer itself.

Mass Balance Calculations from Tracer Concentration Gradients within Cell 5b

We checked the technique, assumptions, and calculations of the tracer deployment by volume-weighting the concentration data gathered internally in Cell 5b one day after the injection. At that time, Li was found in well-defined, high concentration pockets on the eastern side of the limerock berm (Figure 8). We determined the mass of Li in the water on this date by first counting the number of cells in ArcView represented by each discrete concentration (Table 7) and multiplying by the cell area (384 m²) to arrive at the total area in Cell 5b occupied by each concentration range. We then multiplied by the average depth (0.86 m) to arrive at a total volume for each concentration range, which was then multiplied by the average Li concentration for that range (Table 7). Summing the Li mass for each concentration range across the entire concentration gradient produced an independent measure of the Li mass injected into Cell 5b the prior day.

Using this independent measure, we can account for 92% of the injected Li mass. This provides strong evidence that we had made no errors in either calculating the mass of tracer injected or in the tracer delivery and distribution system.

Table 7. Volume-weighted lithium mass interpolated from spatial lithium concentration gradients that were derived from the first day of internal sampling after injecting 1,186 kg of Li as LiCl into Cell 5b (see Figure 8). The average water depth was 0.86m. The background Li concentration of 36 µg/L has been subtracted from the average measured Li concentration.

| Li Concentration Range (µg/L) | Cell Count | Area (m²) | Average concentration (µg/L) | Volume (m³) | Mass (kg) |
|--|-------------------|------------------------------|---|-----------------------------------|----------------------|
| <36 | 17580 | 6,119,907 | | 5,263,120 | |
| 36-50 | 430 | 149,691 | 8 | 128,734 | 1 |
| 50-100 | 823 | 286,501 | 40 | 246,391 | 10 |
| 100-200 | 1417 | 493,283 | 115 | 424,223 | 49 |
| 200-400 | 2184 | 760,289 | 265 | 653,848 | 173 |
| 400-600 | 1549 | 539,234 | 465 | 463,741 | 216 |
| 600-800 | 1566 | 545,152 | 665 | 468,831 | 312 |
| 800-1000 | 600 | 208,871 | 865 | 179,629 | 155 |
| 1000-1200 | 378 | 131,588 | 1065 | 113,166 | 121 |
| 1200-1500 | 130 | 45,255 | 1315 | 38,920 | 51 |
| Total | 26657 | 9,279,771[†] | | 7,980,603 | 1087 |

† 2,293 acres

Flow Calibrations for G-306

Water flow is an important component in determining the hydraulic residence time (HRT) of a wetland. Flow also must be accurately measured when arriving at the percent of tracer injected that is recovered at the outflow. If surface flow measurements are accurate, then any differences between the mass of tracer injected and measured at the outflow must be due to either chemical (e.g., adsorption) or hydrologic (e.g., recirculation, seepage) processes. Our review of the flow data indicates that the supply water was fed at a relatively consistent rate into Cell 5b during the study, with no significant hydrologic losses such as seepage (Table 2).

The one flow discrepancy noted during the study was the poor agreement among DBE, Sutron, and the uncorrected District measurements at G-306 (Table 5). For the one day (March 10, 2004) when measurements were made by all three entities, Sutron's measured flows were higher than DBE's tracer-based flow rate, which in turn were higher than the District-calculated flow rate. We believe that DBE's instantaneous flow rates may have been an underestimate due to physical characteristics of the outflow structures. Because of the high flow velocities through the G-306 levee and the deep downstream canal, the appearance of the dye cloud could not be

discerned from shore until it had passed well beyond the end of the outflow culvert. This resulted in an artificially long transit time, and consequently, lower calculated flow rate than had we been able to accurately discern the dye cloud at the end of the outflow culvert. As noted previously, District flow rates during the tracer study period have since been corrected, using the Sutron data for re-calibration purposes (Table 2).

Given the calibrated and concordant flow rates among G-302, G-304, G-306, and G-310 (Table 2), and G-305 (Table 3), there is very little likelihood that flow discrepancies could have contributed to the appearance of the secondary peak in the tracer concentration profile (Figure 12).

History of Lithium Background Concentrations in STA-1W

Another possible explanation for the bimodal Li tracer profile was that elevated Li concentrations entered into STA-1W in the runoff waters from the watershed during the 14-day tracer-monitoring period. Although we did not measure Li levels in inflow waters at G-305 during the monitoring period itself, Cell 5 background Li concentrations ranged from < 10 to 13 µg/L one month prior to the injection, and were 12 µg/L two days after the end of the monitoring period on March 17, 2004 (Table 8).

In order to explore the possibility of a brief, two-week pulse in Li from the watershed, we evaluated historical Li data for STA-1W. DBE and other entities have conducted numerous Li tracer studies within STA-1W since 1999. Background Li concentrations were measured in all of these studies as part of the tracer injection efforts. Table 8 lists the Li background concentrations of the inflow and outflow waters for various research platforms (bench-scale, mesocosms, test cells, and treatment cells) where tracer experiments were conducted within the footprint of STA-1W.

In addition to the periodically measured Li background concentrations shown in Table 8, DBE compiled two long-term Li background data sets for Cell 1 in STA-1W. The first was twice-a-week sampling of the inflow and outflow waters over 5 months in 2001, where the Li concentration never exceeded 17 µg/L. The second data set represented weekly to bi-weekly

sampling of the surface waters at three stations within Cell 1 during 2003. For that 10-month database, Li concentrations never exceeded 21 µg/L. All the background data for STA-1W waters indicate that Li concentrations never exceeded 50 µg/L, which is considerably lower than the 107 µg/L associated with the secondary peak exiting Cell 5b at G-306 on March 14th (Figure 12). Hence, it is very unlikely that the source of the Li contained within the secondary peak originated as a brief pulse from surface waters in the watershed.

Table 8. Background lithium concentrations for historical tracer studies in STA-1W.

| Location | Date | Background Conc (µg/L) | Reference |
|------------------------------|--------------|-------------------------------|---------------------|
| Beaker Study (Cell 1 water) | 6/4-6/10/01 | <10-16 | DBE Unpublished |
| Post-BMP Mesocosms | 6/14-7/9/01 | <10 | DBE Unpublished |
| Post-BMP Mesocosms | 3/17-4/30/99 | 11-19 | DBE 1999 |
| Post-BMP LR Beds | 3/17-4/30/99 | 12-14 | DBE 1999 |
| Porta-PSTA | | 25-36 | CH2MHill 2000 |
| South Test Cells | | 29-37 | CH2MHill 2000 |
| South Test Cells | | 42 | SFWMD Unpublished |
| South Test Cells | | 32-35 | SFWMD Unpublished |
| South Test Cells | | 38-50 | SFWMD Unpublished |
| South Test Cells | | 21-22 | SFWMD Unpublished |
| STC-1 | March 2001 | 18 | DBE Unpublished |
| STC-1 | 7/29/04 | 14 | DBE Unpublished |
| STC-1 | 7/13/01 | 15 | DBE Unpublished |
| Triple Tracer – Cell 1 South | 3/7/01 | 48 | SFWMD Unpublished |
| Triple Tracer – Cell 5 North | 3/7/01 | 48 | SFWMD Unpublished |
| North Test Cells | | 26-27 | SFWMD Unpublished |
| North Test Cells | | 41 | SFWMD Unpublished |
| NTC-5 | March 2001 | 11-16 | DBE Unpublished |
| NTC-5 | 7/2/04 | 14 | DBE Unpublished |
| NTC-5 | 7/9/04 | 16 | DBE Unpublished |
| Post-BMP Mesocosms | 3/19/04 | 12 | DBE Unpublished |
| Cell 5 Inflow (G304) | 2/3/04 | 13 | DBE Unpublished |
| Cell 5 Mid (G305) | 2/3/04 | 12 | DBE Unpublished |
| Within Cell 5 | 2/3/04 | <10 | DBE Unpublished |
| Cell 5 Outflow G306A-J | 3/2/04 | 28-31 | Cell5b Tracer Study |
| Cell 1 Out | 12/2/01 | 11 | DBE 2003 |
| Cell 2 Out | 12/2/01 | <10 | DBE 2003 |

Quality of the Analytical Chemistry

For this study, Li analyses were performed by a subcontract laboratory (PPB, Inc.) to DBE. To ensure that the subcontract lab provided accurate Li analyses, we performed an external audit of the lab by splitting some of the samples and performing the analysis ourselves using the identical methodology (SM 3111B).

The split sample analyses were performed on waters collected near the first peak of the tracer response curve (Figure 12). The comparison between the results showed close agreement between the laboratories (Table 9), suggesting that analytical error probably did not account for the high Li concentrations found in the secondary peak of the tracer response curve.

Table 9. Comparison of results from the split-sampling audit.

| Log # | Station | Date | ? t (hrs) | Li Concentration (µg/L) | | % rsd |
|--------|------------|--------|-----------|-------------------------|-----------|-------|
| | | | | PPB, Inc. | DBE, Inc. | |
| W24399 | G-306G | 3/7/04 | 80 | 238 | 246 | 2.3 |
| W24400 | G-306G dup | 3/7/04 | 80 | 235 | 243 | 2.4 |
| W24377 | G-306F | 3/7/04 | 88 | 262 | 254 | 2.2 |
| W24381 | G-306F | 3/7/04 | 96 | 224 | 229 | 1.6 |

Recirculating Flow Path

Internal to Cell 5b

The two-dimensional, time-series of the tracer concentration gradients within Cell 5b indicate that there were no significant recirculating pathways inside the cell (Figure 8). This is shown best at day 3 when most of the injected tracer mass was located west of the limerock berm and very little tracer was observed east of the berm.

STA-1W and WCA-1

Since the appearance of the secondary peak is a classic indicator of recirculation, there is strong likelihood that the recirculation pathway occurred outside of the STA. Figure 7 depicts the flow path that the tracer associated with primary peak in Figure 12 would have followed after being released at G306. After exiting G306, the tracer mass would have flowed south to G310, exiting STA-1W into WCA-1. A deep canal (L7) runs along the western boundary of WCA-1 (Figure 7). Structure G-301, which controls north-south flow at this location, was open during

the study period. Flows measured at this structure (to the north) were 87% of those entering into G-302 (Table 2), so it is distinctly possible that the discharge from G-310 could have been routed along the L7 Canal and returned to Cell 5 via G-301 and G-302 (Figure 7).

To determine if a tracer pulse corresponding to the first (primary) tracer peak in Figure 12 could have accounted for the secondary tracer peak 7.3 days later, we estimated the travel time of the peak concentration, T_p , and the magnitude of the unit-peak concentration, C_{up} (Jobson 1996). The time of passage from the leading edge of a concentration peak to a point where the concentration has been reduced to 10 percent of the peak concentration, T_{d10} , can be estimated from the equation:

$$T_{d10} = (2 \times 10^6) / C_{up} \quad (8)$$

where the unit peak concentration is equal to:

$$C_{up} = (1 \times 10^6)(C_p / M_r)(Q) \quad (9)$$

M_r is the mass of tracer recovered (mg) and Q is the volumetric flow rate (L/sec).

We can test the validity of Eq (8) for the hydraulic conditions existing in Cell 5b during the tracer study by determining if the computed travel time for T_{d10} closely approximates the measured travel time for the primary peak in Figure 12. The highest Li concentration (C_p) in the primary peak was 251 $\mu\text{g/L}$, which according to Equation (9) yields a C_{up} of 4.60 sec^{-1} . According to Equation (8), a C_{up} would produce a travel time duration, T_{d10} , of 5.0 days. This compares very favorably with the 5.3 days measured in Figure 12, and thus verifies the suitability of Eq. (8) to the data set.

Having verified that Eq. (8) accurately predicted the travel time for the primary peak, we next applied the equation to determine the theoretical return time for the primary peak if it had been recirculated from STA -1W into WCA-1 and back into Cell 5, so that it would again appear at G-306 as a secondary peak. The maximum concentration observed for the secondary peak was 107 $\mu\text{g Li/L}$ (Figure 12), which is comparable to a C_{up} of 2.37 sec^{-1} based on the mass of tracer recovered of 1006 kg and a flow rate of 2.23×10^4 L/sec. This corresponds to a travel time of 9.8 days according to Eq. (8), which is within 2% of the field-measured travel time (10 days) for the secondary peak (with tail extrapolated by exponential fit). These data provide us with a

theoretical basis for confirming that the secondary peak could have been caused by a recirculation of the primary peak through the L7 canal in WCA-1.

Another independent approach in determining the plausibility of the secondary peak being caused by the recirculation of the primary peak outside the STA-1W footprint is to calculate retention times of each pathway based on their volumes and flows (Table 10). Summing the retention times of the component pathways should yield the time of arrival at G-306 of the secondary peak after the departure of the primary peak from the same control structure.

Table 10. The estimated time of arrival of the secondary lithium (Li) peak at G-306 due to Li mass associated with the primary peak being recirculated around the perimeter of STA-1W and re-entering Cell 5 via the G-301 and G-302 control structures. Flow rates are District averages for the two-week period of the tracer test (March 3-17, 2004); the volumes were determined from stage levels and dimensions (length x width) obtained from the District and Daroub et al. (2002).

| Recycle Pathway | Volume (x 10⁶ m³) | Flow (m³/day) | Time of Arrival (hours) |
|---------------------------|--|-------------------------------------|------------------------------------|
| G-306 to G310 | 3.800 | 21.3 | 49.5 |
| G-310 to G-301 (L7 Canal) | 2.044 | 19.4 | 29.2 |
| G-304 to G-305 (Cell 5a) | 1.893 | 21.9 | 24.0 |
| G-305 to G-306 (Cell 5b) | 7.98 | 22.3 | 99.4 |
| Total | | | 202.1 hr or 8.4 days |

The estimated arrival time between the two peaks (8.4 days) corresponds fairly well to the measured arrival time of 7.3 days, again suggesting that the recirculation flow path outside of the STA-1W footprint caused the appearance of the secondary tracer peak at G-306.

Tracer Mass Balance

We injected a total lithium mass of 1168 kg at G-305, and based on G-306 flow and Li concentration data, retrieved 1212 kg, resulting in a 104% recovery. Uncertainty in the flow measurements at G306 within $\pm 10\%$ likely contributed to the Li mass recovery exceeding 100%. The interference by the recirculated secondary Li peak, which appeared at G-306 before the descending limb of the primary peak reached background Li concentrations, also likely introduced some error into our outflow Li mass estimates (Figure 12).

Tracer Hydraulic Retention Time (HRT)

The measured HRT for Cell 5b was 4.35 days, which is nearly the same as the nominal HRT of 4.15 days. This indicates that “on average”, the entire wetland volume was being utilized for treatment.

Hydraulic Effects of the Limerock Berm

At present, the effects of the LR berm on the hydraulics of Cell 5b can only be estimated, since no tracer studies were performed prior to its construction. In lieu of such tracer comparison studies (i.e., pre- and post-LR berm), some insight can be gained by examining both the Li concentrations observed adjacent to the LR berm during the internal sampling events, and the manner in which the Li exited the outflow culverts throughout the monitoring period. We also evaluated overall hydraulic characteristics of Cell 5b, and compared these with results from previous tracer studies in other cells of STA-1W.

Limerock Berm (Internal) Sampling Results

Internal sampling in Cell 5b was performed on days 1, 3, and 7 after LiCl injection. The sampling grid adjacent to the LR berm was more resolute than the sampling grid for Cell 5b as a whole. The resolution for the 50 stations on both sides of the berm was 25 meters (Figures 13 - 15). Throughout the monitoring period the water level was approximately 10 cm above the berm.

The day 1 sampling data demonstrate that the Li tracer initially reached the southern part of the berm at two locations (Figure 13). These stations appear to lie on a hydraulic short-circuit within the cell, since we observed a shallow, relic farm canal containing little SAV upstream (to the east) of the berm. At these stations, Li concentrations were high both upstream and downstream of the berm (Figure 13), indicating that under the conditions of this study (10 cm water depth above the berm), the berm doesn't totally eliminate short-circuiting effects by redistributing flow. A similar pattern was observed for the day 7 sampling event upon appearance of the second tracer peak: highest Li concentrations were again observed at the same stations as on day 1, with both upstream and downstream sides of the berm exhibiting high Li concentrations (Figure 14).

Day 1

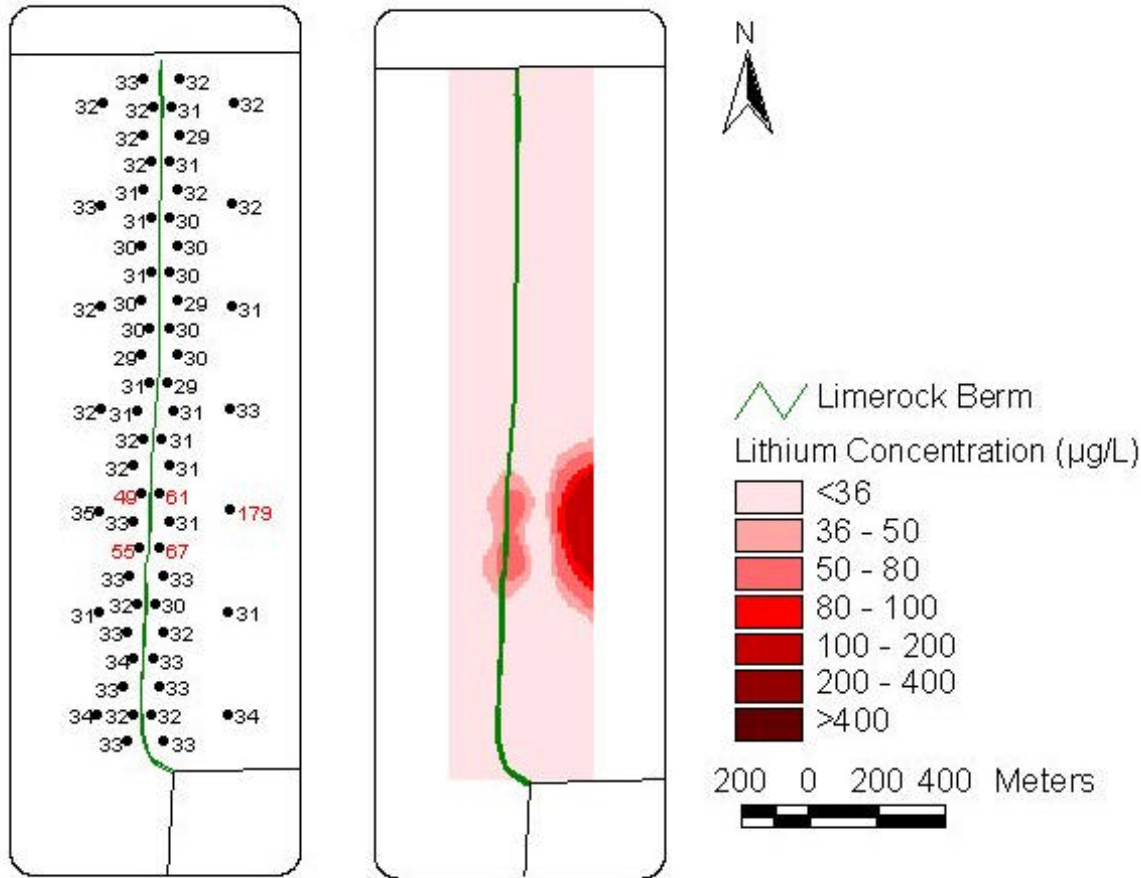


Figure 13. Two-dimensional spatial gradients comparing the lithium concentrations for water samples collected at mid depth (0.3 m) in Cell 5b one day after LiCl was injected at 22 culverts along the G-305 levee. Actual Li concentration values ($\mu\text{g/L}$) are provided in the figure to the left. The sampling nodes adjacent to the LR berm are situated at a distance of 25 m from each other.

Day 7

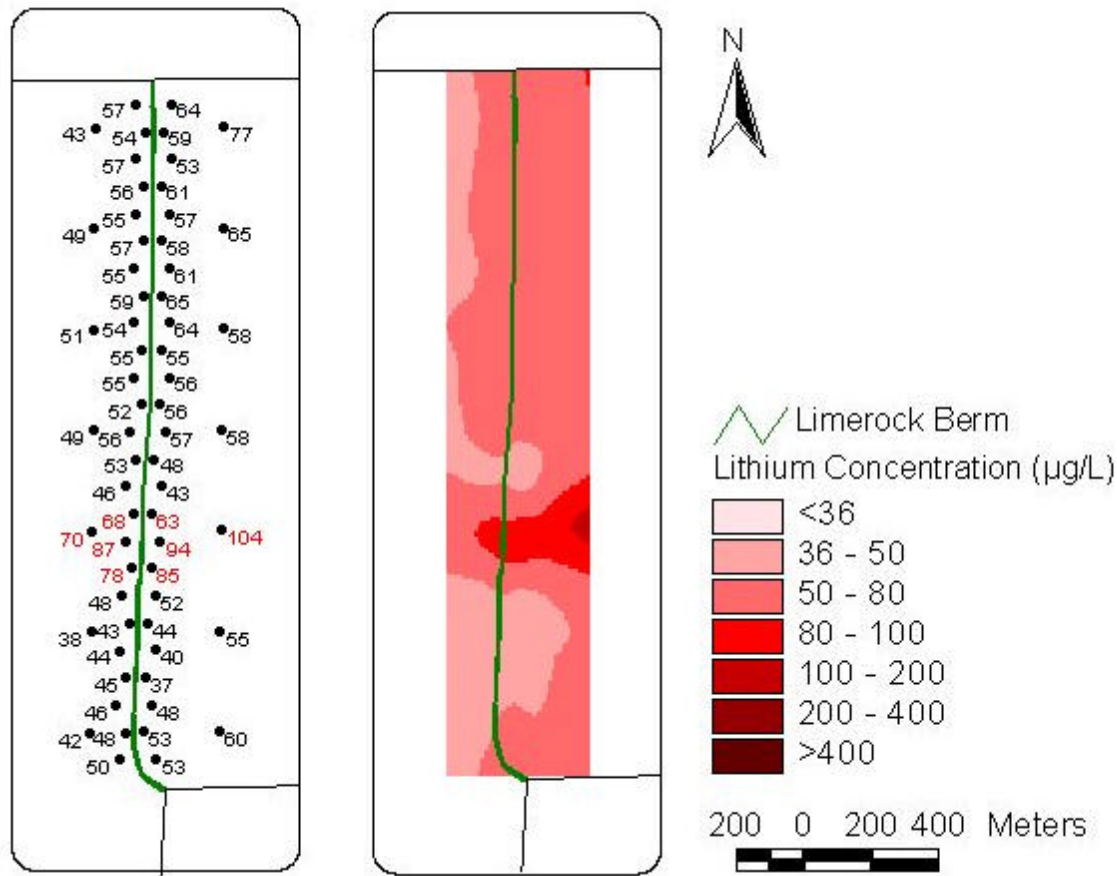


Figure 14. Two-dimensional spatial gradients comparing the lithium concentrations for water samples collected at mid depth (0.3 m) in Cell 5b seven days after LiCl was injected at 22 culverts along the G-305 levee. Actual Li concentration values ($\mu\text{g/L}$) are provided in the figure to the left. The sampling nodes adjacent to the LR berm are situated at a distance of 25 m from each other.

Day 3

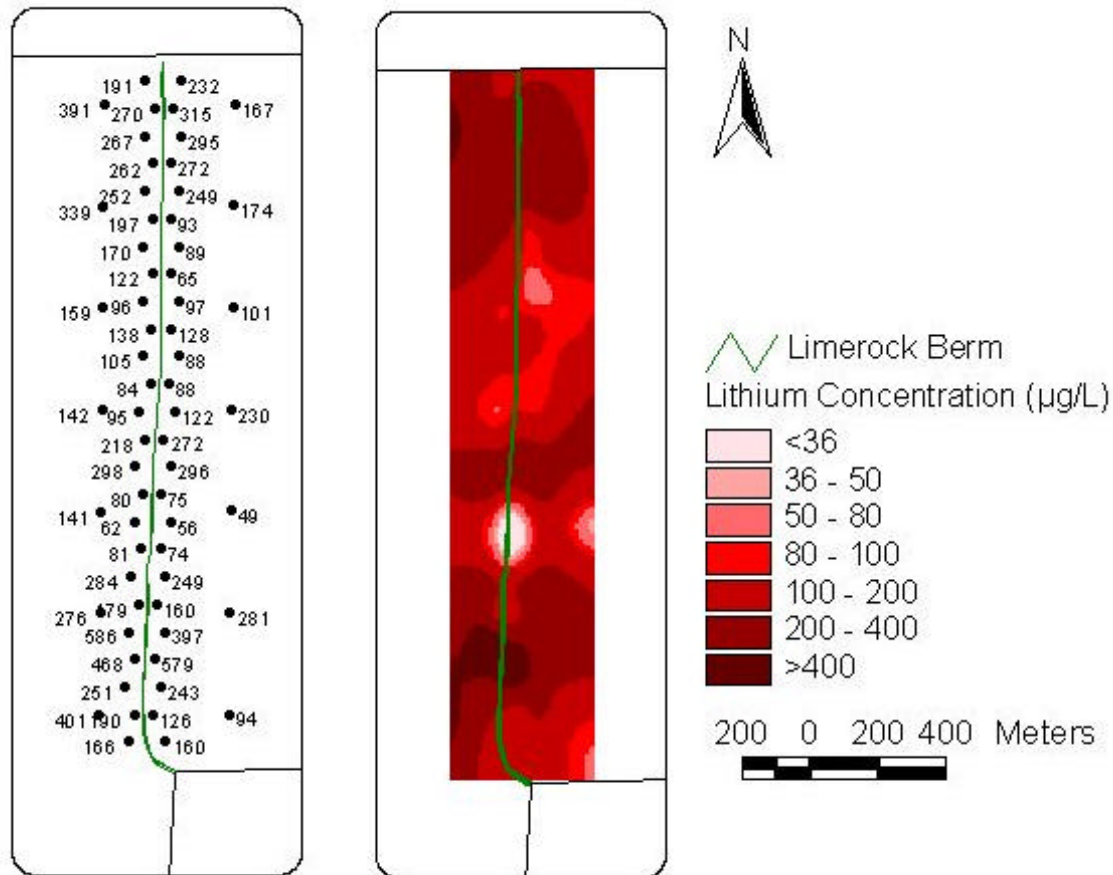


Figure 15. Two-dimensional spatial gradients comparing the lithium concentrations for water samples collected at mid depth (0.3 m) in Cell 5b three days after LiCl was injected at 22 culverts along the G-305 levee. Actual Li concentration values ($\mu\text{g/L}$) are provided in the figure to the left. The sampling nodes adjacent to the LR berm are situated at a distance of 25 m from each other.

On day 3, the Li concentrations generally show comparable concentrations both upstream and downstream of the berm (Figure 15). This pattern can also be seen in the isoclines and indicate that the presence of the berm had little or no effect on flow distribution immediately adjacent to the berm.

Outflow (G306) Monitoring Results

By the end of the monitoring period, each of the ten culverts at G306 exported $10 \pm 2\%$ of the Li tracer, indicating a fairly even distribution of tracer within the cell. It should be noted however, that the individual culvert tracer response curves (Figure 11) behaved differently from one other. The tracer first reached the G306 levee at culvert F on 3/5 @ 7:00, followed shortly by culvert G at 15:00 (Table 6). The second Li tracer peak also first reached the G306 levee at these same two culverts (Table 6). Culverts F and G are slightly south of the area where the tracer first reached the mid-cell berm on both day 1 and day 7 after injection. These observations suggest that a preferential flow-path continued to exist at this location after flow passed through the berm.

Another difference observed in the individual culvert tracer response curves is that the peaks for culverts C, D, and E occurred approximately at the same time, were of shorter duration, and achieved a higher concentration than the other culverts. The peaks at the rest of the culverts tended to be lower in concentration, but of longer duration (Figure 11). These culverts (C, D and E) align spatially with the high Li concentration area observed in the day 1 sampling event east of the berm (Figure 8). This could be viewed as an indication that a large mass of tracer passed through the cell along a preferential flow path and was not effectively redistributed by the berm.

Comparison with Previous Tracer Study Results

Another method of gaining insight into the effect of the berm is to compare results from this study with previous tracer studies conducted within two other STA-1W wetlands, neither of which contain a limerock berm. This comparison is rendered difficult, however, because each STA-1W cell exhibits unique physical characteristics that likely influence tracer behavior. The two studies we used for comparison were the STA-1W Cell 4 rhodamine-WT tracer study

conducted in December 1999 (DBE 2002) and the STA-1W Cell 1 Li tracer study performed in December 2001 (DBE 2003).

The STA-1W Cell 4 tracer evaluation was similar to that of Cell 5b in two respects: the tracer was injected through a series of inflow culverts that were equally spaced across the inflow levee (five culverts for Cell 4; 22 culverts for Cell 5); and both cells are SAV-dominated wetlands. However, at the time of the Cell 4 study, this wetland had two predominant short-circuits caused by deep channels along the eastern and western levees of the cell (Figure 16). The tracer assessment of Cell 4 documented that the wetland was hydraulically impaired, with pronounced short-circuiting and a very low TIS value of 1.3. The presence of these pronounced short-circuits therefore renders comparisons difficult.

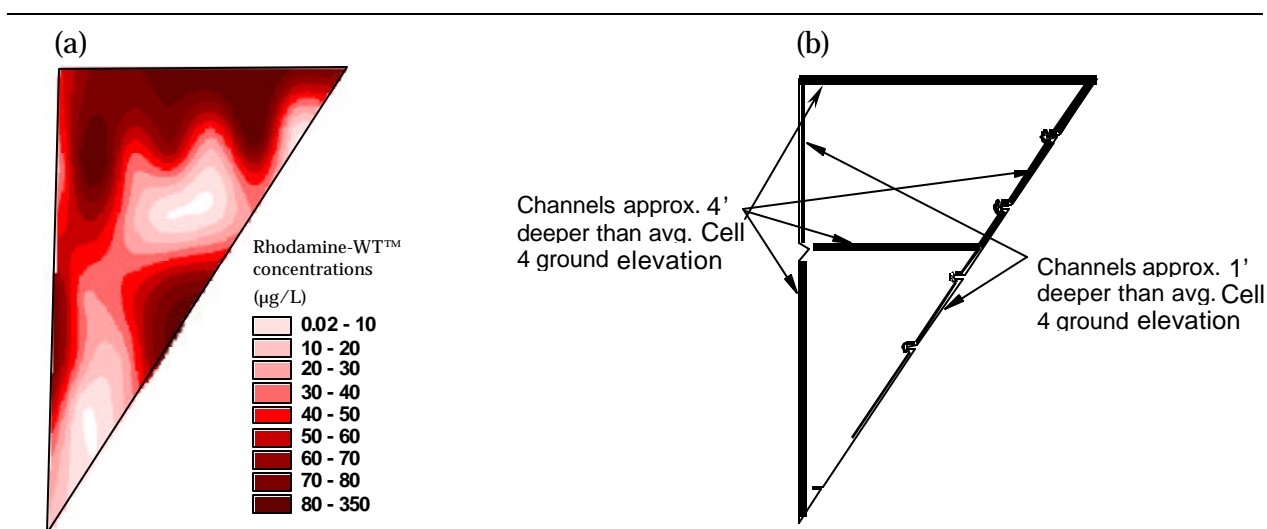


Figure 16. (a) Two-dimensional spatial concentration gradient 27 hours after the injection of Rhodamine-WT™ dye into STA-1W Cell 4 on December 16, 1999, depicting short-circuits along the eastern and western borders of the cell. These short-circuits were caused by channels (b) documented during a field survey conducted at the time of the study.

In contrast to both Cells 4 and 5b, inflow waters feed into STA-1W Cell 1 primarily at one location, at the northwest corner of the cell adjacent to structure G-255. To characterize the hydraulic behavior of Cell 1, we injected the Li tracer upstream of G-255 at the G-303 structure. As expected, we observed that approximately 90% of the tracer entered Cell 1 at the northwestern corner (Figure 17). Perhaps due to this focused inflow location, the

temporal/spatial characterization of the progression of Li through the cell indicated a preferential flow path down the western boundary of the cell (Figure 17). This preferential flow was also observed at the ten outflow culverts, where the four westernmost culverts (A-D) not only received the tracer first, but ultimately conveyed 68% of the total Li mass out of the cell (Figure 18).

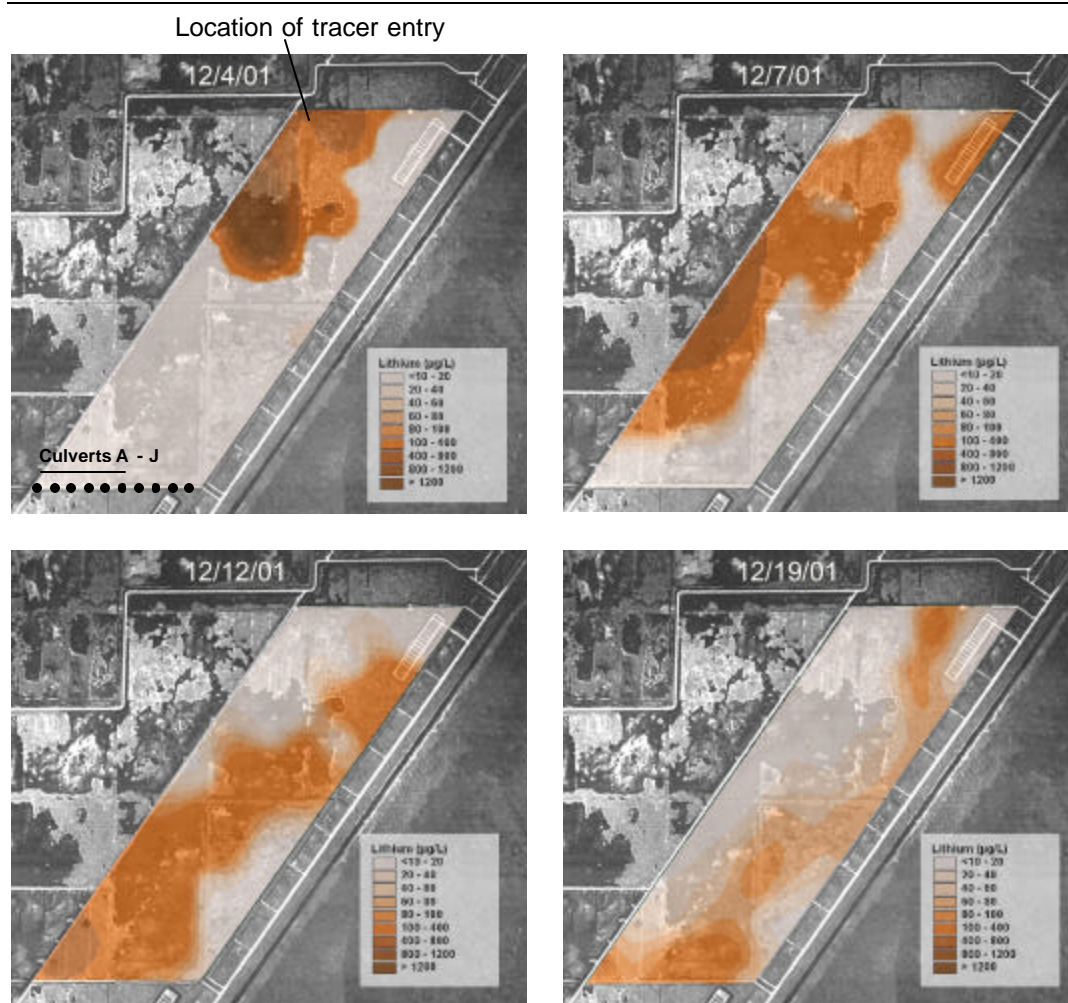


Figure 17. Spatial characterization of lithium concentrations in December 2001 superimposed on an enhanced aerial photo of Cell 1 on four sampling dates (2, 5, 10, and 17 days after tracer injection). The aerial photo was provided by the District.

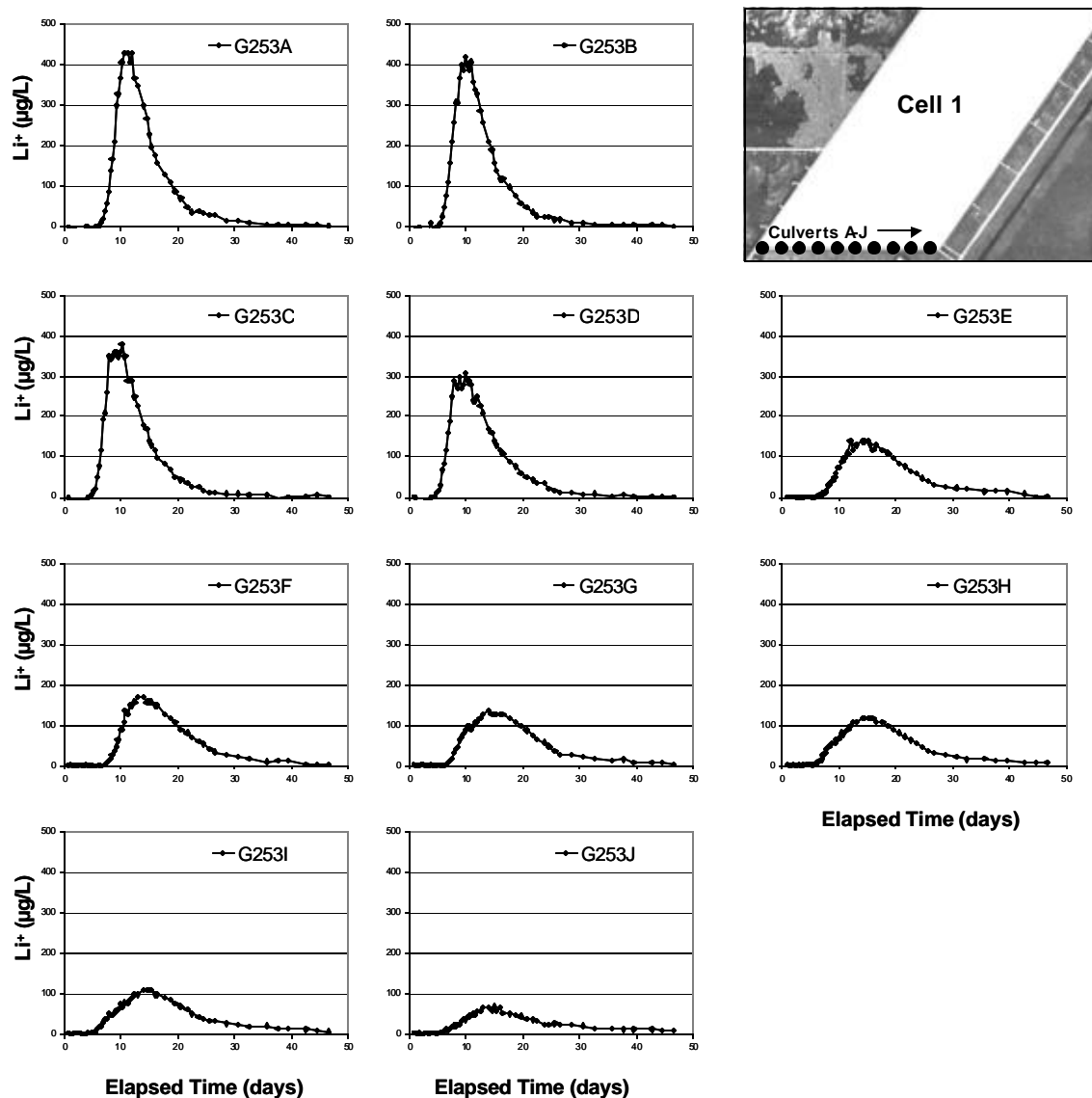


Figure 18. Tracer response curves for G-253 culverts A – J at the outflow of STA-1W Cell 1.

While the comparisons of the Cell 5b study with the prior assessments in Cells 1 and 4 are limited due to the factors noted above, these comparisons make one factor quite clear: Cell 5b displays remarkably efficient hydraulic characteristics. For example, the tanks-in-series (TIS) value calculated for Cell 5b using the method of moments was 10.6, an extraordinarily high value when compared to previous assessments, both in STA-1W (TIS of 1.3 for Cell 4; TIS of 3.4 for Cell 1; and TIS of 2.8 for Cell 2) and in other wetlands (DBE 2003; Kadlec and Knight 1996).

This high hydraulic efficiency can also be seen in the “near-plug-flow” shape of Cell 5’s outflow tracer response curve (Figure 12), as well as the comparable export, on a mass basis, of Li from all 10 outflow culverts (Figure 11). Cell 5b’s high efficiency is probably due to effective distribution of inflows among the 22 culverts at G-305, as well as the absence of pronounced short-circuit pathways. The limerock berm undoubtedly also plays a role in enhancing hydraulic performance of the wetland, but its exact contribution cannot be elucidated from the findings of this study.

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Appendices

Appendix A

LiCl injection calculation

Appendix B

Flow velocity measurements at G-305 on 3/2/04

Appendix C

Field Logs

Appendix D (electronic copy only)

DataReportEDD.xls: all raw data for this project

FieldQASummary.xls: summary tables of field QC

DB-031004-Hardcopy.pdf: PPB report for samples received on 3/10/04. Includes laboratory QC results

DB-031904-Hardcopy.pdf: PPB report for samples received on 3/19/04. Includes laboratory QC results

DB-040804-Hardcopy.pdf: PPB report for samples received on 4/8/04. Includes laboratory QC results

Appendix A

Calculations to determine the amount of LiCl to be injected into Cell 5b of STA-1W at a target concentration of 150 mg Li/L

Area is 2293 acres (928 ha) and water depth estimated as 0.8 m.

Volume of Cell 5b = $(9.28 \times 10^6 \text{ m}^2) (0.8 \text{ m}) = 7.42 \times 10^6 \text{ m}^3$

Target Li concentration is **150 mg/L:**

Mass needed: $(0.15 \text{ mg Li/L})(7.42 \times 10^6 \text{ m}^3)(10^{-6} \text{ kg/mg})(10^3 \text{ L/m}^3) = \mathbf{1113 \text{ kg Li}}$

Volume needed: $(1113 \text{ kg Li}) / (0.08024 \text{ kg Li/L of solution}) = \mathbf{13,871 \text{ L LiCl solution}}$

No. of 55-gal barrels required: $(13,871 \text{ L}) / [(55 \text{ gal/barrel})(3.785 \text{ L/gal})] = \mathbf{66.6 \text{ barrels}}$

Appendix B

Flow velocity for the 22 culverts (A–V) at G-305. Rhodamine-WT measurements were made on March 2, 2004, the day before the LiCl injection.

| Culvert | Culvert Length ft | Rhodamine travel time sec | Adjusted* Rhodamine travel time sec | culvert Flow ft/sec |
|----------------|----------------------------------|--|--|------------------------------------|
| A | 91 | 134 | 127.5 | 0.71 |
| B | 91 | 142 | 134.6 | 0.68 |
| C | 92 | 107 | 100.3 | 0.92 |
| D | 95 | 127 | 119.6 | 0.79 |
| E | 91 | 118 | 110.1 | 0.83 |
| F | 90.5 | 121 | 114.1 | 0.79 |
| G | 90 | 107 | 100.1 | 0.90 |
| H | 90 | 97 | 89.1 | 1.01 |
| I | 90.5 | 113 | 105.7 | 0.86 |
| J | 91 | 114 | 107.3 | 0.85 |
| K | 90 | 101 | 94.1 | 0.96 |
| L | 90 | 86 | 77.9 | 1.16 |
| M | 90.5 | 91 | 84.3 | 1.07 |
| N | 90.5 | 78 | 69.5 | 1.30 |
| O | 91 | 90 | 81.5 | 1.12 |
| P | 90 | 89 | 82.3 | 1.09 |
| Q | 91 | 92 | 86.2 | 1.06 |
| R | 85.333 | 95 | 88.3 | 0.97 |
| S | 91 | 84.5 | 77.6 | 1.17 |
| T | 91.5 | 83.5 | 77.8 | 1.18 |
| U | 91.5 | 91 | 85.3 | 1.07 |
| V | 88.167 | 94 | 86.7 | 1.02 |

* The transit time for the dye to travel from the collection bucket to the end of the delivery pipe (Figure 3) has been subtracted from the total travel time.

Appendix C: Field logs